

Bond Orbitals and Bond Energy in Elementary Phosphorus

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A discussion of the relative stability of the P_4 molecule and black phosphorus is carried out, with use of hybrid spd bond orbitals. The amount of strain in the P_4 molecule, in which the bond angles are 60° , is calculated to be $22.8 \text{ kcal mole}^{-1}$. This value is shown to be compatible with thermochemical data; it corresponds to the value $51.3 \text{ kcal mole}^{-1}$ for the bond energy of the normal P—P bond. A structure is proposed for red phosphorus and other allotropic forms of the element, and some of their properties are discussed in relation to their structure.

INTRODUCTION

AN interesting problem in chemical bond theory is offered by the relative stability of the P_4 molecule. In this molecule the four phosphorus atoms are at the corners of a regular tetrahedron, each being bonded to the other three; there are accordingly three 60° P—P—P bond angles per phosphorus atom. The strain associated with these small bond angles might be expected to be rather large: the strain energy for three 60° C—C—C bond angles in cyclopropane is $22 \text{ kcal mole}^{-1}$, and a similar amount of strain energy per phosphorus atom would not be surprising. In fact, however, the strain energy is smaller, the difference in enthalpy¹ of ordinary white phosphorus (PIII) and the stable form, black phosphorus, being $10.3 \text{ kcal mole}^{-1}$. The form of white phosphorus which is stable at temperatures below -77°C , PIV, has enthalpy only $8.9 \text{ kcal mole}^{-1}$ greater than that of black phosphorus, and it would be predicted that a still denser form of P_4 , with increased van der Waals attraction between the molecules, corresponding to that operating in the denser black phosphorus, would show a still smaller difference in enthalpy from black phosphorus. An argument given below, based on the correction of the enthalpy of black phosphorus for van der Waals attractions and repulsions, leads to the conclusion that the bent-bond strain energy in the P_4 molecule is about $5.7 \text{ kcal mole}^{-1}$ per phosphorus atom, or $22.8 \text{ kcal mole}^{-1}$ per P_4 molecule.

A theoretical treatment of strain energy in this molecule was carried out by Moffitt,² who assumed the bonds in the molecule to be formed with use of pure $3p$ orbitals. Moffitt found the strain energy calculated by his quantum-mechanical treatment to be $11.8 \text{ kcal mole}^{-1}$ per P—P bond, or $17.7 \text{ kcal mole}^{-1}$ per phosphorus atom. He decreased this value by 40 percent, to $10.6 \text{ kcal mole}^{-1}$ per phosphorus atom, by making an empirical correction based on the lack of agreement with experiment given by a similar calculation for cyclopropane. The agreement of his uncorrected value with

the experimental strain energy, which we estimate to be $5.7 \text{ kcal mole}^{-1}$ per phosphorus atom, is not good.

Arnold³ has suggested that the phosphorus atoms in the P_4 molecule use pd^2 hybrid orbitals in forming bonds. He pointed out that pd^2 bond orbitals have strength 2.29, and normal bond angles of $66^\circ 26'$, so that very little strain would be required to distort them to 60° . However, this suggestion cannot be accepted. The energy of promotion of a $3p$ electron to a $3d$ orbital in the phosphorus atom is given by spectroscopic data as about $194 \text{ kcal mole}^{-1}$. In order for a phosphorus atom to form three d^2p bonds, two electrons would need to be promoted in this way, which would confer upon the molecule an instability of $388 \text{ kcal mole}^{-1}$ per phosphorus atom.

We have treated the problem by the consideration of spd hybrid bond orbitals, the hybridization parameters being selected so as to minimize the energy of the molecule, including the bond energy and the atomic energy. We have obtained for the strain energy of the P_4 molecule, relative to a hypothetical P_4 molecule with normal bonds, the value $22.8 \text{ kcal mole}^{-1}$, or $5.7 \text{ kcal mole}^{-1}$ per phosphorus atom. This value seems to be in good agreement with experiment. The hybrid bond orbitals, which have strength 2.0074 in the bond direction (considerably greater than the value 1.6304 for pure p orbitals), are largely p in character, the contribution of the $3s$ orbital amounting to 0.4 percent and that of the $3d$ orbital to 2.2 percent.

HYBRID ORBITALS IN P_4

We assume that the energy of a P—P bond is proportional to the square of the strength of the bond orbital in the bond direction. This postulate for bent bonds was proposed originally by R. Spitzer,⁴ and was applied by him in the discussion of cyclopropane, spiropentane, and other molecules,^{5,6} for which good agreement with experiment was found. If the bonds formed by the phosphorus atom were pure $3p$ bonds, with $S^2=3$ in the direction of maximum bond strength and $S^2=2.658$ in the direction corresponding to 60° bond

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¹ Thermochemical data used in this paper are from Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Standards, 1950.

² W. E. Moffitt, Trans. Faraday Soc. 44, 987 (1948).

³ J. R. Arnold, J. Chem. Phys. 14, 351 (1946).

⁴ R. Spitzer, Ph.D. thesis, Cal. Inst. tech., 1941.

⁵ J. E. Kilpatrick and R. Spitzer, J. Chem. Phys. 14, 463 (1946).

⁶ G. L. Humphrey and R. Spitzer, J. Chem. Phys. 18, 902 (1950).

angles ($19^\circ 28'$ from the best bond direction), the calculated strain energy would be about 10 kcal mole⁻¹ per phosphorus atom. The calculation is made in the following way. The heat of dissociation of P₄ into 4P corresponds to a P—P average bond energy⁷ of 47.5 kcal mole⁻¹. If this is set proportional to S^2 in the bond direction (2.658), and the corresponding value is calculated for $S^2=3$, it is found to be 53.6 kcal mole⁻¹, indicating the strain energy to be about 6.1 kcal mole⁻¹ per bond, or 9.2 kcal mole⁻¹ per phosphorus atom, there being $1\frac{1}{2}$ bonds per atom in the P₄ molecule.

The calculated strain energy is decreased somewhat by the consideration of spd hybridization. Only a small amount of s and d character would be expected for the bond orbitals, because of the large promotion energy associated with the transfer of an electron from a $3p$ orbital to a $3d$ orbital, or from a $3s$ orbital to a $3p$ orbital. Pure p bonds would be formed by an atom in the configuration $3s^2 3p^3$. The inclusion of $3s$ character in a bond orbital would require a contribution of the configuration $3s 3p^4$, and the inclusion of $3d$ character in the bond orbital would require a contribution of the configuration $3s^2 3p^2 3d$. We have used the value 194 kcal mole⁻¹ for the excitation energy of both configuration $3s 3p^4$ and configuration $3s^2 3p^2 3d$ of phosphorus.⁸ (The lowest states of the configurations $3s 3p^4$ and $3s^2 3p^2 3d$ lie above the lowest state of $3s^2 3p^3$ by 170 kcal mole⁻¹ and 200 kcal mole⁻¹, respectively, and the estimated valence states is 186 kcal mole⁻¹.) The energy per half of a P—P bond can be expressed approximately by the equation

$$W = -7.13S^2 + 194(a^2 + c^2) \text{ kcal mole}^{-1}. \quad (1)$$

In this equation S is the strength in the bond direction in the P₄ molecule of a hybrid bond orbital $as + bp + cd$. The first term represents the bond energy for the half bond, and the second term the energy of promotion of the electron associated with the s and d character of the hybrid bond orbital. The factor 7.13 was chosen to lead to essentially the experimental value for the bond energy.

It was found possible to minimize W with respect to the parameters of a general spd wave function, of the form

$$\psi = \sum_{i=1}^9 a_i \psi_i, \quad (2)$$

in which the successive functions $\psi_1 \cdots \psi_9$ are s , p_x , d_z , p_y , d_{x+z} , d_{xy} , p_z , d_{y+z} , and d_{x+y} , respectively. Three equivalent bonds of this character related to one another by rotation through 120° around the z axis may be formed; the orthogonality and normalization conditions then require the following relations among the

coefficients of the orbital for the bond in the xz plane:

$$\begin{aligned} a_1^2 + a_2^2 + a_3^2 &= \frac{1}{3}, \\ a_4^2 + a_5^2 + a_6^2 &= \frac{2}{3}, \\ a_7 &= a_8 = a_9 = 0. \end{aligned}$$

It was found on solution of this problem that the best bond orbitals have the form

$$\psi_1 = 0.0622s + 0.5694p_x + 0.0695d_z + 0.8096p_z + 0.1230d_{x+z} + 0.0435d_{xy} \quad (3)$$

with ψ_2 and ψ_3 similar. The strength of these orbitals in the bond direction for P₄ is 2.0074, and the value of W is -23.75 kcal mole⁻¹.

A similar calculation can be made for arbitrary bond direction. The procedure for finding the best spd hybrid bond orbital with promotion energies as given above is that of solving the secular equation for the function $\psi = as + bp_x + cd_z$. This secular equation has the form⁹

$$\begin{vmatrix} Q - W - \alpha & -\sqrt{3}\alpha & -(5)^{\frac{1}{2}}\alpha \\ -\sqrt{3}\alpha & -W - 3\alpha & -(15)^{\frac{1}{2}}\alpha \\ -(5)^{\frac{1}{2}}\alpha & -(15)^{\frac{1}{2}}\alpha & Q - W - 5\alpha \end{vmatrix} = 0 \quad (4)$$

in which $Q = 194$ kcal mole⁻¹ and $\alpha = 7.13$ kcal mole⁻¹. Solution of this equation leads to

$$\psi = 0.0685s + 0.9858p_x + 0.1530d_z$$

with $S = 2.118$ and $W = -26.55$ kcal mole⁻¹. The bond angle corresponding to these best spd hybrid bond orbitals for phosphorus is $89^\circ 55'$. The prediction would accordingly be made that the normal bond angles for phosphorus should be close to 90° .

THE NORMAL PHOSPHORUS-PHOSPHORUS BOND

The difference in the values of W found for unstrained bonds and for 60° bond angles is 2.80 kcal mole⁻¹ per half-bond, or 8.40 kcal mole⁻¹ per phosphorus atom. This value may accordingly be taken as the calculated strain energy per phosphorus atom in P₄, relative to a hypothetical P₄ molecule with unstrained bonds. The calculated strain energy per P₄ molecule is 33.6 kcal mole⁻¹.

We are, however, primarily interested in the energy of the normal P—P bond. A normal P—P bond may be defined as the phosphorus-phosphorus bond in a substance in which the bond angles have normal values. The normal value of the angle between two bonds formed by a phosphorus atom is about 101° ; representative values are 99° and 102° in black phosphorus, 100.5° in phosphorus trichloride, 101.5° in phosphorus tribromide, and 102° in phosphorus tri-iodide. The increase over the value $89^\circ 55'$, at which the strength of the bond orbitals is a maximum, is to be attributed to the van der Waals repulsion of the ligated atoms. (A smaller bond angle, 93° , is observed in phosphine; presumably the van der Waals repulsion of the hydrogen atoms is so

⁷ F. S. Dainton, Trans. Faraday Soc. **43**, 244 (1947).

⁸ Charlotte E. Moore, Atomic Energy Levels, Circular, Natl. Bur. Standards, 467 (1949).

⁹ L. Pauling, Proc. Roy. Soc. (London) **A196**, 343 (1949).

much less than that of larger atoms as to cause only a 3° increase in bond angle.) A calculation similar to that described above for the strain energy for bond angle 60° leads to the value 0.75 kcal mole⁻¹ as the strain energy per 101° bond angle. Two phosphorus atoms bonded to a third also experience van der Waals attraction and van der Waals repulsion. The energy quantities per 101° bond angle calculated by use of the equations given in the following section, with the constant α of Eq. (7) (for van der Waals repulsion) chosen so as to lead to equilibrium with the forces of bond angle strain and van der Waals attraction at 101°, have the values -2.29 kcal mole⁻¹ and 2.44 kcal mole⁻¹, respectively. The total bond angle strain energy for angle 101° is thus 0.90 kcal mole⁻¹ per bond angle, or 2.70 kcal mole⁻¹ per phosphorus atom.

We may use this quantity and the calculated strain energy for P₄ to obtain the strain energy of P₄ relative to a molecule containing normal P-P bonds, with the normal amount of strain. This value is 8.40-2.70=5.70 kcal mole⁻¹ per phosphorus atom, or 22.8 kcal mole⁻¹ per P₄ molecule, and the energy of a normal P-P bond is calculated to be 47.5+ $\frac{1}{6}$ ·22.8=51.3 kcal mole⁻¹.

THE ENTHALPY OF BLACK PHOSPHORUS

Gaseous P₄ has enthalpy 3.12 kcal mole⁻¹ per phosphorus atom, relative to white phosphorus III, and it is accordingly greater in enthalpy than black phosphorus by 13.4 kcal mole⁻¹. Black phosphorus is the only modification of phosphorus whose crystal structure is known.¹⁰ Each phosphorus atom is bonded to three other phosphorus atoms, at 2.20Å, essentially the same bond distance as in the P₄ molecule. The bonded phosphorus atoms form puckered sheets, with P-P-P bond angles lying between 99° and 102°.

We may use the thermochemical data for black phosphorus as the basis for predicting the energy of a hypothetical P₄ molecule in which there are normal bonds, by correcting for the van der Waals attraction and repulsion in the black phosphorus crystal.

The energy of van der Waals attraction between phosphorus atoms other than those connected directly by bonds can be calculated by use of the London equation. The London equation for van der Waals attraction is

$$E_{\text{att}} = -\frac{3}{2} \frac{\alpha_A \alpha_B I_A I_B}{r_{AB}^6 (I_A + I_B)} \quad (5)$$

in which α_A and α_B are the polarizabilities of atoms A and B, at the distance r_{AB} apart, and I_A and I_B are the average energies of excitation, usually taken as equal to the ionization energies of the neutral atoms. It is found empirically, by consideration of the heats of sublimation of crystals of the noble gases, that this equation gives too small values of the van der Waals attraction, if I_A

and I_B are taken as the ionization energies, and that improved agreement with experiment is obtained by multiplying by the factor 1.57. We accordingly make use of the equation

$$E_{\text{att}} = -4.26 \frac{R_A R_B I_A I_B}{r_{AB}^6 \frac{1}{2}(I_A + I_B)} \text{ kcal mole}^{-1} \quad (6)$$

in which R_A and R_B are the mole refractions, in cm³, I_A and I_B are the ionization energies in electron volts, and r_{AB} is the interatomic distance in Å. For phosphorus the mole refraction has the value 8.70 cm³, and the ionization energy the value 11.0 ev. The interatomic distances in black phosphorus according to the structure reported by Hultgren, Gingrich, and Warren,¹⁰ in addition to the bond distances, are 3.31 (2), 3.41 (2), 3.43 (4), 3.68 (2), 3.87 (2), 3.98 (2), 4.14 (1), 4.40 (2), etc. The application of Eq. (6) to these data, with an integration from 4.9Å to infinity to give the contributions of the larger distances, leads to -10.2 kcal mole⁻¹ as the energy of van der Waals attraction of atoms other than bonded atoms and next-bonded atoms (P...P) in black phosphorus.



The reason for excluding the next-bonded atoms (2 at 3.31 and 4 at 3.43Å) is given below.

Consideration must also be given to the energy of van der Waals repulsion. In general, the energy of van der Waals repulsion between atoms can be expressed approximately by an equation of the form

$$E_{\text{rep}} = \alpha e^{-3.35 r_{AB}} \quad (7)$$

In black phosphorus the repulsion between two phosphorus atoms bonded to the same third atom is sufficiently great not only to overcome the van der Waals attraction but also to overcome the tendency of the P-P-P bond angle to assume the normal value 89°55', the angle being increased to 99° (for one bond angle) and 102° (for the other two). The nonbonded distances that are involved are 3.31Å and 3.43Å, respectively. It is found that when the constant α is adjusted in such a way as to give equilibrium at these bond angles, with the force of van der Waals repulsion just counterbalancing that of van der Waals attraction and of bond strain, the energy of van der Waals repulsion is 7.32 kcal mole⁻¹ and that of van der Waals attraction is -6.87 kcal mole⁻¹ per phosphorus atom. These values have been used in a calculation described in the preceding section.

In addition, the puckered layers of phosphorus atoms are superimposed, the atomic contacts between layers being those at 3.68 and 3.87Å. Also there are two contacts at 3.41Å, for which the force of van der Waals attraction must be counterbalanced by a repulsive force. It is easily shown that the ratio of the energy of the van der Waals repulsion (given by Eq. (7)) to the energy of van der Waals attraction at the equilibrium distance r_{AB} is -6/3.35 r_{AB} , and that for these contacts

¹⁰ Hultgren, Gingrich, and Warren, J. Chem. Phys. 3, 351 (1945).

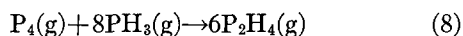
the van der Waals repulsion energy amounts to 2.4 kcal mole⁻¹ per phosphorus atom.

Thus we calculate that there are in black phosphorus a stabilizing energy of van der Waals attraction, other than between bonded and next-bonded atoms, amounting to -10.2 kcal mole⁻¹, and a destabilizing energy of 2.4 kcal mole⁻¹ in van der Waals repulsion, resulting in an over-all stabilization of -7.8 kcal mole⁻¹ per phosphorus atom. From this calculation the enthalpy of a hypothetical form of phosphorus in which there are normal bonds and the only interactions effective are those between each atom and its three ligates and between these ligates is -10.3+7.8=-2.5 kcal mole⁻¹ per phosphorus atom, relative to the standard state, white phosphorus. The enthalpy of gaseous P₄ is +3.3 kcal mole⁻¹ per phosphorus atom, relative to the same standard state, so that the strain energy in P₄, relative to the hypothetical state with unstrained bonds, is given as 2.5+3.3=5.8 kcal mole⁻¹.

This value corresponds to the value 23.2 kcal mole⁻¹ per P₄ molecule for the strain energy relative to a molecule containing normal P-P bonds.

THE HEAT OF HYDROGENATION OF PHOSPHORUS

We may use data for the heat of hydrogenation of phosphorus to phosphine and to solid phosphorus hydride, (P₂H)_n, to evaluate the strain energy of the P₄ molecule. Unfortunately the heat of formation of diphosphorus tetrahydride, P₂H₄, has not been determined. If it were known, the strain energy of the P₄ molecule could be calculated simply as the heat evolved by the reaction

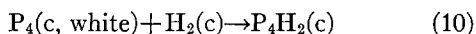


Since phosphorus and hydrogen have the same electronegativity, we would expect the heat of the reaction



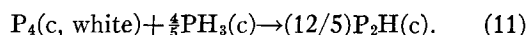
to be zero, except for the strain energy of the P₄ molecule. The observed heat of this reaction, 21.7 kcal mole⁻¹, thus provides a value of this strain energy.

It is likely that the hydride (P₂H)_n, which is formed (together with phosphine) by photochemical decomposition of diphosphorus tetrahydride and by many other reactions, contains normal P-P bonds. If the van der Waals energy in (P₂H)_n(c) is equal to that in the crystalline elements, the heat of the reaction



would be the strain energy in the P₄ molecule. The observed value is 24.0 kcal mole⁻¹.

A value of the strain energy not dependent on the assumption of zero energy of partial ionic character of the P-H bond is the heat of the reaction



The observed value (involving the estimate 0.6 kcal

mole⁻¹ for the heat of fusion of phosphine) is 24.6 kcal mole⁻¹.

We may summarize the values of the strain energy of the P₄ molecule relative to a hypothetical molecule with normal P-P bonds as follows:

Bond orbital calculation	22.8 kcal mole ⁻¹
Enthalpy of black phosphorus	23.2
Heat of reaction 9	21.7
Heat of reaction 10	24.0
Heat of reaction 11	24.6

None of these values can be considered to have great accuracy; nevertheless, their approximate agreement suggests that they are not in great error. It is gratifying that the average of the thermochemical values is close to the value given by the bond orbital calculation. We accordingly accept 22.8 kcal mole⁻¹ as the strain energy of the P₄ molecule, and 51.3 kcal mole⁻¹ as the bond energy of a normal P-P bond.

THE ENTHALPY OF WHITE PHOSPHORUS

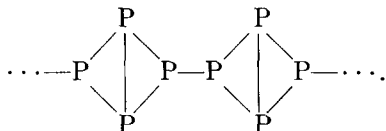
We may use the expressions for the van der Waals energy of attraction and repulsion to evaluate the enthalpy of white phosphorus. Although the structure of white phosphorus has not been determined, it is likely that it consists of P₄ molecules which in the form stable at room temperature are in essentially free rotation. The density of the crystal is 1.83 g cm⁻³, which corresponds to a distance between centers of molecules of 5.41Å, assuming the molecules to be arranged in cubic closest packing. The energy of van der Waals attraction, using the formula given above and the factor 8.61 for the number of effective contacts, is 19.36 kcal mole⁻¹ per P₄ molecule, or 4.84 kcal mole⁻¹ per phosphorus atom. The energy of van der Waals repulsion, assumed to be of the form $\alpha e^{-3.35r_{AB}}$, is 33.2 percent of this, so that the effective energy of stabilization in the crystal is calculated to be 3.23 kcal mole⁻¹. This value is in excellent agreement with the experimental value for the heat of sublimation of phosphorus III, which is 3.28 kcal mole⁻¹.

THE NATURE OF RED PHOSPHORUS AND AMORPHOUS BLACK PHOSPHORUS

The structure of red phosphorus has not been determined. Hultgren, Gingrich, and Warren¹⁰ made x-ray photographs of ordinary "amorphous" red phosphorus, which showed diffuse rings on the powder pattern, and also of crystalline red phosphorus, and prepared radial distribution curves from them. These curves are similar in character to those of black phosphorus, showing that each atom has three bonded ligates at about 2.2Å, and several nonbonded neighbors at distances from 3.5 to 4Å. There are a smaller number of neighbors at the 101° bond angle distance, 3.4Å, in red phosphorus than in black crystalline phosphorus, and a larger number at about 4Å.

We suggest that red phosphorus is formed from white phosphorus by the rupture of only one bond in each P₄ tetrahedron. This would permit the P₄ group to open

out into a figure formed by two equilateral triangles with a common base. The two apical phosphorus atoms would then form bonds with similar phosphorus atoms in adjacent P_4 complexes, and presumably long chains of bonded atoms would be formed in this way, with a structure such as



Half of the phosphorus atoms would form bonds with two 60° bond angles and one 101° bond angle, and the other half of the atoms would form bonds with one 60° bond angle and two 101° bond angles. The average number of 60° bond angles would then be $\frac{3}{2}$ per phosphorus atom, rather than 3 as in white phosphorus, and 0 as in black phosphorus. It is obvious that this structure would correspond to an enthalpy value about midway between that of white phosphorus and black phosphorus. The enthalpy of red phosphorus is in fact -4.4 , that of black being -10.3 kcal mole $^{-1}$, relative to white phosphorus. The ease of formation of red phosphorus from white phosphorus, in comparison with the formation of black phosphorus, is explained by the fact that only one bond per P_4 molecule needs to be broken in the formation of red phosphorus, whereas three of the six bonds need to be broken for the formation of black phosphorus. Black phosphorus, although it is the most stable known form of the element at normal conditions, has not been reported to have been made except by application of high pressure.

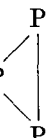
RATES OF REACTION

A more detailed discussion may be given of the tendency of different forms of phosphorus to occur. The vapor of phosphorus at not too high temperature consists of P_4 molecules. When the vapor is condensed white phosphorus is formed, without change in molecular structure from the vapor. In order for the more stable solid forms of the element to appear, a reaction must take place in which P—P bonds in the P_4 molecules are broken and new bonds are formed. The activation energy for this process is expected to be high, and hence it is not surprising that the conversion of white phosphorus to red phosphorus is slow.

The rate of conversion of white phosphorus to a form containing chains of the type described above (or similar rings) would be predicted to be much faster than the conversion of this form (red phosphorus) to black phosphorus, for the following reason. Let E^* be the activation energy for the conversion of white phosphorus to red phosphorus. This process, as postulated, involves breaking one P—P bond in a tetrahedral P_4 molecule and the conversion of six 60° bond angles into bond angles of about 100° . The strain energy for six 60° bond angles has been evaluated above as about 11.4 kcal mole $^{-1}$, relative to normal bonds, and this strain energy

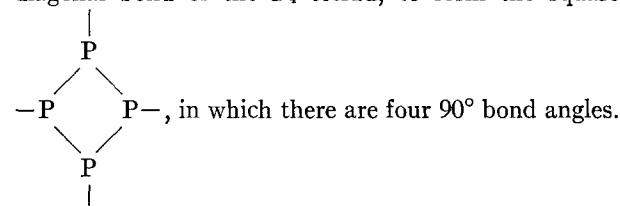
would be expected to decrease E^* below the value for unstrained bonds. We have estimated the bond energy for an unstrained P—P bond to be 51.3 kcal mole $^{-1}$, and we would expect this value to be the heat of activation for a reaction involving rupture of such bonds. The heat of activation for the formation of red phosphorus may hence be predicted to be $51.3 - 11.4 = 39.9$ kcal mole $^{-1}$. An experimental value¹¹ is 38.7 kcal mole $^{-1}$, in good agreement with the predicted value.

This calculation depends on the assumption that the strain energy of the 60° bond angles in red phosphorus, with the configuration shown above, is the same, per 60° angle, as that of the 60° bond angles in the tetrahedral P_4 molecule. We may check this assumption in the following way. The strain energy per half bond may be taken as a function of the angle between the bond direction and the direction in which the bond orbital would have its maximum strength. For the P_4 molecule this angle is $19^\circ 28'$, and for a phosphorus atom forming

bonds of the type  it is 15° . If we assume pro-

portionality of the strain energy to the square of the cosine of this angle (as is true for pure p bonds) the calculated strain energies per 60° bond angle differ by only 15 percent. When the strain energy of the normal bonds is taken into consideration the difference becomes smaller still, and it seems likely that little error is introduced by the assumption that the strain energy can be represented purely as a function of the bond angle values.

To convert red phosphorus into other forms the easiest step can be predicted to be the rupture of the diagonal bond of the P_4 tetrad, to form the square



In the Bridgman process of making black phosphorus it seems that the temperature rises enough to break other bonds, so that the four-membered rings are not preserved. Crystalline black phosphorus has never been made except by Bridgman's methods,¹² using high pressure (with or without shear) and elevated temperature. It seems likely that the success of the method with pressure around 15,000 atmos and initial temperature around 200°C is due to the heating of the reacting material by the evolved heat of reaction, which for an adiabatic system would cause a temperature increase of

¹¹ T. W. DeWitt and S. Skolnik, J. Am. Chem. Soc. **68**, 2305 (1946).

¹² P. W. Bridgman, J. Am. Chem. Soc. **36**, 1344 (1914); **38**, 609 (1916).

over 1500°. We can understand why red phosphorus cannot be converted into black phosphorus simply by heating it. At 300°C its rate of conversion into black phosphorus can be predicted to be very slow, the rate constant calculated by assuming the rate to be the same as for the formation of red phosphorus, as observed by DeWitt and Skolnik, except with activation energy 46 kcal mole⁻¹ instead of 38.7 kcal mole⁻¹ being 1×10^{-5} min⁻¹. Hence months would be required for the conversion into black phosphorus at this temperature, at which, however, the vapor pressure of red phosphorus is appreciable (about 0.06 atmos), so that, unless confined, it would be converted into gas and would escape.

The material called amorphous black phosphorus¹³ is formed from white phosphorus at pressures about 12,000 atmos and initial temperatures about 200°C. These pressures and temperatures are somewhat lower than those at which crystalline black phosphorus is formed, and the temperatures are lower than those at which red phosphorus is rapidly made at 1 atmos pressure. The

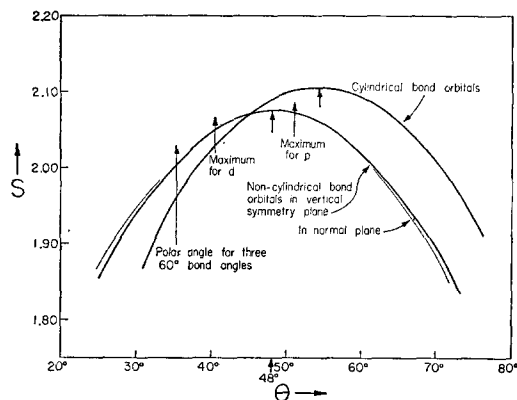


FIG. 1. Strength of bond orbitals for phosphorus as function of polar angle.

reaction is slow to start and evidently speeds up because of the heating of the reacting material.

The density of amorphous black phosphorus is reported to be about 2.25 g cm⁻³, whereas that of crystalline black phosphorus, which is formed at higher temperatures and pressures, is 2.69 g cm⁻³, and that of red phosphorus is 2.34 g cm⁻³. The enthalpy of amorphous black phosphorus is indicated by Jacobs' thermochemical measurements to be near that of red phosphorus. We think that it is likely that Jacobs' amorphous black phosphorus is to be classed with red phosphorus and violet phosphorus, and that its structure involves chains of the same type. In its formation, as in the formation of red phosphorus and violet phosphorus from white phosphorus, only one of the six bonds in the P₄ tetrahedron needs to be broken. Jacobs has reported that by long heating at 125°C amorphous black phosphorus is converted into violet phosphorus.

¹³ R. B. Jacobs, J. Chem. Phys. **5**, 945 (1937).

NONCYLINDRICAL *SPD* BOND ORBITALS

In the first discussion of hybrid bond orbitals¹⁴ the *spd* hybrid orbitals that were discussed—the best *spd* orbitals, two equivalent *spd* orbitals involving one *d* orbital, four *ds**p*² square orbitals, four best tetrahedral orbitals, and six *d*²*s**p*³ octahedral orbitals—all have cylindrical symmetry about the bond axis, and in his more general discussion of *spd* hybridization Hultgren¹⁵ found it convenient to restrict his treatment to similar cylindrically symmetrical orbitals. In the study of P₄ we first carried out a calculation of strain energy for three equivalent cylindrical bond orbitals, and found the best cylindrical orbitals for a phosphorus atom with 60° bond angles to be of the form $0.070s + 0.990p + 0.125d$, with $W = -19.59$ kcal mole⁻¹, the calculated strain energy being 11.04 kcal mole⁻¹ per phosphorus atom. The calculation was then carried out with noncylindrical orbitals, resulting in a decrease in the calculated strain energy by 33 percent, to 7.38 kcal mole⁻¹. It is evident that in refined calculations the approximation of assuming the bond orbitals to have cylindrical symmetry should not be made without consideration of the magnitude of the error that might be introduced.

It is of interest to consider the reason for the superiority of noncylindrical orbitals over cylindrical orbitals for the problem under discussion. The strength of the best orbital (Eq. 3) in its vertical symmetry plane is shown as a function of the polar angle ϑ in Fig. 1. The value of ϑ at the bond direction is 35°16', and the maximum strength is at $\vartheta = 48°10'$.

The strength at various angles from the direction of the maximum in a plane normal to the vertical symmetry plane is indicated by the two arcs just above (for small ϑ) and below (for large ϑ) the curve for the symmetry plane. It is evident from the proximity of the arcs and the curve that the noncylindrical orbital deviates only slightly from cylindrical symmetry, and that the explanation of its superiority must be elsewhere.

The explanation is to be found by the comparison of the orbital with the cylindrically symmetrical orbital with the same amounts of *s* and *p* character. The three orthogonal orbitals of this type have their maximum strength at $\vartheta = 54°25'$, with the strength changing with angle as shown in Fig. 1. It is seen that although the maximum strength ($S = 2.1071$) is greater than that of the noncylindrical orbital ($S = 2.0744$), the strength in the direction of the P₄ bonds is much less (1.960 instead of 2.0074). The desirable properties of the noncylindrical orbitals are achieved by having the maximum contribution of the *p* part of the orbital at a larger polar angle ($\vartheta = 54°53'$) than that of the *d* part ($\vartheta = 36°20'$). In this way the three orbitals are kept orthogonal while the strength in the 60°-bond directions is increased.

¹⁴ L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

¹⁵ R. Hultgren, Phys. Rev. **40**, 891 (1932).